



SiO₂/styrene butadiene rubber-coated poly(ethylene terephthalate) nonwoven composite separators for safer lithium-ion batteries

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ABSTRACT :

We develop a new nonwoven composite separator for a safer lithium-ion battery, which is based on coating of silica (SiO₂) colloidal particles/styrene-butadiene rubber (SBR) binder to a poly(ethylene terephthalate) (PET) nonwoven support. The SiO₂ particles are interconnected by the SBR binder and closely packed in the nonwoven composite separator, which thus allows for the development of unusual porous structure, i.e. highly-connected interstitial voids formed between the SiO₂ particles. The PET nonwoven serves as a mechanical support that contributes to suppressing thermal shrinkage of the nonwoven composite separator. The SiO₂/SBR content in the nonwoven composite separators plays an important role in determining their separator properties. Porous structure, air permeability, and electrolyte wettability of the nonwoven composite separators, in comparison to a commercialized polyethylene (PE) separator, are elucidated as a function of the SiO₂/SBR content. Based on this understanding of the nonwoven composite separators, the effect of SiO₂/SBR content on the electrochemical performances such as self-discharge, discharge capacity, and discharge C-rate capability of cells assembled with the nonwoven composite separators is investigated.

Keywords : lithium-ion batteries; nonwoven composite separators; silica particles; styrene butadiene rubber; poly(ethylene terephthalate)

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1. Introduction

Currently, most popular separators in lithium-ion batteries are typically made of polyolefins. These separators have many advantages in the viewpoint of practical commercialization, however, their poor thermal shrinkage, low porosity, and inferior electrolyte wettability¹⁻³⁾ have often raised serious concerns about their fundamental functions to ensure the electrical isolation and ionic transport between electrodes.

Among numerous approaches to overcoming these drawbacks of the polyolefin-based separators, the use of nonwovens comprising multi-fibrous layers has drawn considerable attention owing to their excellent thermal

properties, high porosity, and cost competitiveness.⁴⁻¹¹⁾ However, considering that separators for lithium-ion batteries must have sufficiently small pore size and narrow pore size distribution enough to prevent self-discharge and internal short-circuits of cells, excessively large pore size and broad pore size distribution of conventional nonwovens often hinder their successful application to lithium-ion batteries. Several attempts to solve the aforementioned challenges of the nonwovens have been carried out, which include the coating of ceramic powders and polymer binders to nonwovens,^{6,7)} the electrospinning-based nanofiber nonwovens,⁸⁻¹⁰⁾ and the impregnation of gel-polymer electrolytes into nonwovens.¹¹⁾

Meanwhile, close-packed arrangements of colloidal particles have shown great potential as an ideal starting template for preparation of micro- and nanostructured porous materials that could be used in various applica-

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tions such as sensors, catalysts, and photonic crystal devices.¹²⁻¹⁴ In the present study, by using the concept of these colloidal structures, we develop a new nonwoven composite separator for a lithium-ion battery. This is based on coating of silica (SiO₂) colloidal particles/styrene-butadiene rubber (SBR) binder to a poly(ethylene terephthalate) (PET) nonwoven support. The nanoparticle arrangement of SiO₂ colloidal particles provides the nonwoven composite separator (hereinafter, referred to as NC separator) with unusual porous structure, i.e. well-connected interstitial voids formed between the close-packed SiO₂ particles being interconnected by SBR binder. Hence, the SiO₂/SBR content in the NC separators is expected to play an important role in determining their membrane properties (particularly, porous structure). Meanwhile, the PET nonwoven serves as a mechanical support^{3,4,6,11} that contributes to suppressing thermal shrinkage of the NC separator.

Porous structure, air permeability (i.e., Gurley value), and liquid electrolyte wettability of the NC separators, in comparison to a commercialized polyethylene (PE) separator, are elucidated as a function of SiO₂/SBR content. Based on this characterization of the NC separators, the effect of SiO₂/SBR content on electrochemical performances such as self-discharge, discharge capacity, and discharge C-rate capability of cells assembled with the NC separators is investigated.

2. Experimental

A coating solution was prepared by mechanically mixing SiO₂ colloidal solution (average particle size = ca. 80 nm) with SBR emulsion for 2 h, where the SBR was employed as a binder for the SiO₂ particles. In an effort to vary the SiO₂/SBR content in the NC separators, two different solid contents (= amount of SiO₂ and SBR) in the coating solutions were employed, which were respectively 15 wt% (hereinafter, the resulting NC separator is referred to as NC separator-low) and 18 wt% (NC separator-high). The SiO₂/SBR ratio in the coating solutions was fixed at 95/5 (wt%/wt%). Meanwhile, the influence of SBR binder on the NC separators is considered to be trivial due to its very small amount relative to the SiO₂ content. A PET nonwoven (thickness = 17 μm) was used as a mechanical/thermal support. The PET nonwoven was soaked into the coating solution for 3 min by dip-coating. The coating solution-immersed PET nonwovens were dried at room temperature, followed by vacuum drying at 60 °C for 4 h. The thicknesses of the NC separators

were observed to be around 17 μm (NC separator-low) and 18 μm (NC separator-high), respectively. Meanwhile, as a control sample, a commercialized PE separator (thickness = 20 μm, Tonen) was chosen.

The surface and cross-sectional morphologies of separators were investigated using field emission scanning electron microscopy (FE-SEM, Hitachi). The air permeability was examined with a Gurley densometer (Gurley), where a low Gurley value (sec 100 cc⁻¹) indicates high air permeability.¹⁻³ For evaluation of electrochemical performance, a liquid electrolyte of 1 M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) = 1/1 v/v (Technosemi Chem) was used. The electrolyte wettability of separators was examined by observing the separator surface immediately after dropping the liquid electrolyte onto the separators. In addition, the electrolyte uptake of separators was determined by measuring the weight difference between the dry state and the electrolyte-swollen state. The electrochemical stability window of separators was estimated by a linear sweep voltammetry experiment performed on a working electrode of stainless-steel and a counter and reference electrode of lithium-metal at a scan rate of 1.0 mV s⁻¹. A unit cell (2032 coin) was assembled by sandwiching a separator between a natural graphite anode and a LiCoO₂ cathode and then activated by filling the liquid electrolyte. The charge/discharge capacities of cells were examined using a cycle tester (PNE Solution). The discharge current densities were varied from 0.1 to 2.0 C at a constant charge current density of 0.2 C under a voltage range of 3.0~4.2 V.

3. Results and discussion

In contrast to a pristine PET nonwoven having excessively large-sized pores that are irregularly formed between the PET nonwoven fibers (Fig. 1(a)), the NC separators show quite a different porous structure (Figs. 1(b)-1(f)). In the NC separators, the pores of PET nonwovens were crammed with the SiO₂ particles/SBR binders. An interesting finding is that in comparison to the NC separator-low (i.e., SiO₂/SBR solid concentration in the coating solution = 15 wt%) (Fig. 1(b)), the NC separator-high (i.e., SiO₂/SBR solid concentration in the coating solution = 18 wt%) allows the incorporation of larger amount of SiO₂ particles between the PET nonwoven fibers, resulting in the more compact packing of SiO₂ particles (Fig. 1(c)). Herein, as a representative example, the porous structure of the NC separator-high was further characterized. The high-magnification

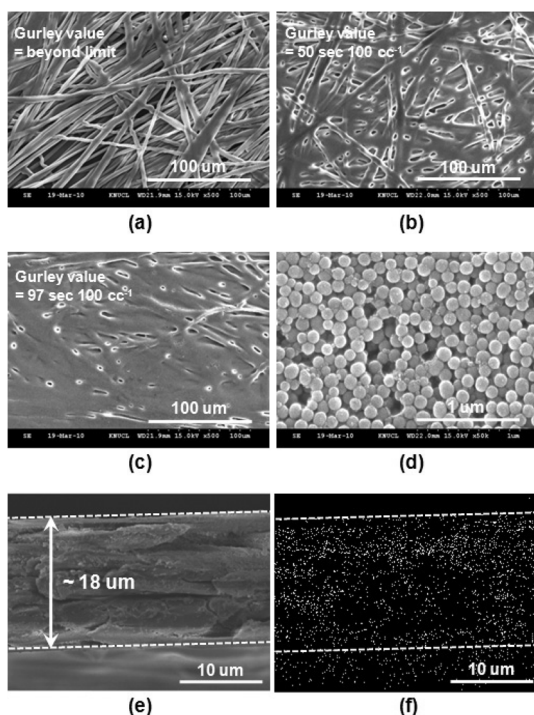


Fig. 1. FE-SEM photographs of: (a) pristine PET nonwoven (surface); (b) NC separator-low (surface); (c) NC separator-high (surface, low-magnification, $\times 500$); (d) NC separator-high (surface, high-magnification, $\times 50,000$); (e) NC separator-high (cross-section). (f) An EDS image of NC separator-high (cross-section).

photograph of the NC separator-high (Fig. 1(d)) apparently demonstrates that the SiO_2 particles in the NC separator-high are closely packed, which consequently contributes to the formation of unique porous structure, i.e. well-connected interstitial voids. The cross-sectional morphology (Fig. 1(e)) of the NC separator-high shows that the SiO_2 particles are compactly embedded between the PET fibers in the thickness direction. This is further confirmed by an EDS image for Si (silicon) elements. Fig. 1(f) depicts that the bright dots signifying the Si elements of SiO_2 particles are uniformly dispersed in the NC separator-high.

The porous structure of the NC separators is quantitatively characterized by measuring its Gurley value. Compared to the PE separator ($= 240 \text{ sec } 100 \text{ cc}^{-1}$), the NC separators presents the low Gurley values ($= 50 \text{ sec } 100 \text{ cc}^{-1}$ for the NC separator-low and $97 \text{ sec } 100 \text{ cc}^{-1}$ for the NC separator-high). This low Gurley value represents high air permeability, which thus indicates

a low resistance for air transport.^{1-7,11)} The Gurley value of the pristine PET nonwoven was too low to be exactly determined, i.e. it was beyond the measuring limit of the instrument, revealing that the pristine PET nonwoven has immoderately large-sized pores. Meanwhile, the relatively lower Gurley value of the NC separator-low confirms that the SiO_2 particles are loosely packed, which is consistent with the previous morphological results (Fig. 1).

Following the aforementioned morphological characterization of the NC separators, other separator properties such as thermal shrinkage, electrolyte wettability, and electrochemical stability window were investigated. Herein, the NC separator-high was compared with the conventional PE separator. The thermal shrinkage of NC separator was compared with that of the PE separator by measuring the (area-based) dimensional change after exposure to 150°C for 0.5 h. Fig. 2(a) shows that the NC separator presents insignificant change in thermal shrinkage, in comparison to the PE separator showing the thermal shrinkage of $\sim 94\%$. The PET nonwoven is thermally stable, because it has a high melting temperature of more than 250°C and does not experience stretching processes that are essentially employed for making a PE separator.¹⁻³⁾

Accordingly, it is believed that the superior thermal stability of the PET nonwoven contributes to preventing the thermal shrinkage of the composite nonwoven separator.

The electrolyte wettability of separators was examined in Fig. 2(b). The NC separator-high is quickly wetted

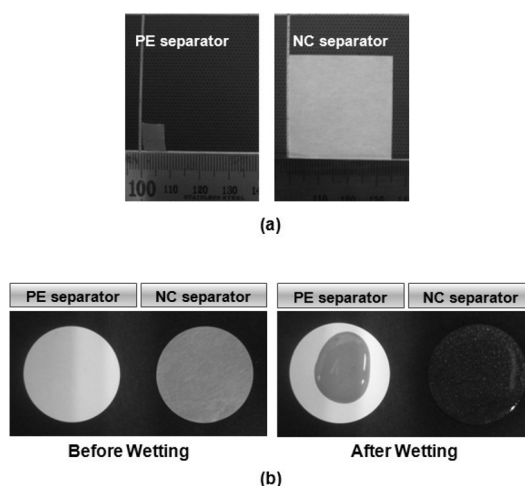


Fig. 2. (a) Thermal shrinkage of PE separator and NC separator-high after exposure to 150°C for 0.5 h. (b) Liquid electrolyte wettability of PE separator and NC separator-high.

by the liquid electrolyte and also affords a larger electrolyte uptake ($\sim 160\%$ vs. $\sim 120\%$ for PE separator). This improvement in the electrolyte wettability of the NC separator is attributed to its relatively polar (i.e., electrolyte-philic) constituents and the well-developed porous structure (i.e., the highly-connected interstitial voids).

The electrochemical stability window of separators was elucidated by measuring linear sweep voltammograms. Fig. 3 shows that the electrochemical stability of the NC separators is comparable to that of a commercialized PE separator and no decomposition of any components below 4.4 V (vs. Li^+/Li) takes place, although the NC separators appear to be oxidized above 4.5 V.

The porous structure of separators is known to critically affect OCV (Open Circuit Voltage) behavior of cells,^{1-3,11} where OCV drop of cells reflects self-discharge and possibly predicts internal short-circuits. A separator with immoderately large-sized pores and nonuniform pore size distribution tends to inadequately prevent leakage current between electrodes, which results in a decline of the OCV. Herein, the cells were charged to 4.2 V and their voltage drop was measured as a function of time. It is of note that there is little difference in the OCV profiles between the NC separator-high and PE separator (Fig. 4). In contrast, the cell assembled with the NC separator-low shows a sharp drop of the OCV. This OCV behavior can be explained by comparing the porous structure of the separators. Previous morphological characterization (Fig. 1) showed that due to the presence of the closely packed SiO_2 particles in the nonwovens, the NC separator-high presents relatively well-tailored porous structure, as compared to the NC separator-low. Hence, it is reasonably expected that the porous structure

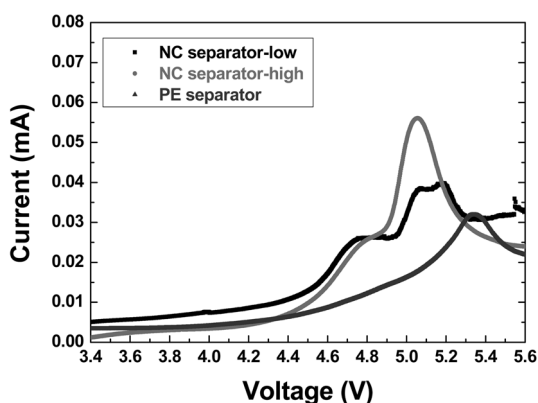


Fig. 3. Linear sweep voltammograms of PE separator and NC separators at a voltage scan rate of 1.0 mV s^{-1} .

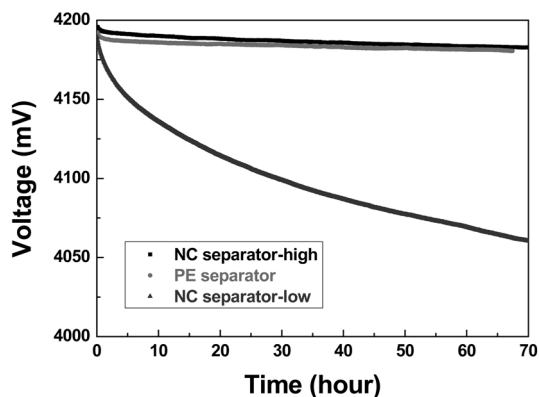


Fig. 4. OCV profiles of cells assembled with PE separator, NC separator-low, and NC-separator-high, wherein the cells are charged to 4.2 V and their voltage drop is measured as a function of time.

of NC separator-high is well-tailored to suppress the self-discharge of cells.

The cell performances of NC separators at various charge/discharge conditions were investigated. Fig. 5(a) shows that under a voltage range of 3.0-4.2 V, the cell assembled with the NC separator-low is difficult to be charged to a predetermined voltage of 4.2 V. After elapse of very long time, the cell manages to reach 4.2 V and then yields a discharge capacity of approximately 138 mAh g^{-1} at a discharge current density of 0.1 C. However, after the 1st cycle, the cell could no longer be charged to 4.2 V. This indicates that the porous structure of the NC separator-low is poorly developed and thus may possibly provoke internal short-circuits between electrodes during the charge/discharge reaction, which is also coherent with the OCV results (Fig. 4).

On the other hand, the NC separator-high (Fig. 5(b)) shows the normal discharge capacities, moreover which are higher than those of the PE separator (Fig. 5(c)). Intriguingly, this difference in the discharge capacities between the separators becomes larger at higher discharge current densities where the influence of ionic transport on ohmic polarization (i.e., IR drop) is more significant.¹⁵⁻¹⁷ Fig. 5(d) summarizes the discharge capacities of the separators as a function of discharge current density (i.e., C-rate). The previous results (Figs. 1 and 2) exhibited that in comparison to the PE separator, the NC separator-high has the low Gurley value indicating highly porous structure and also the large electrolyte uptake. Both the advantages of NC separator-high are expected to allow for the improved discharge C-rate capability. Our

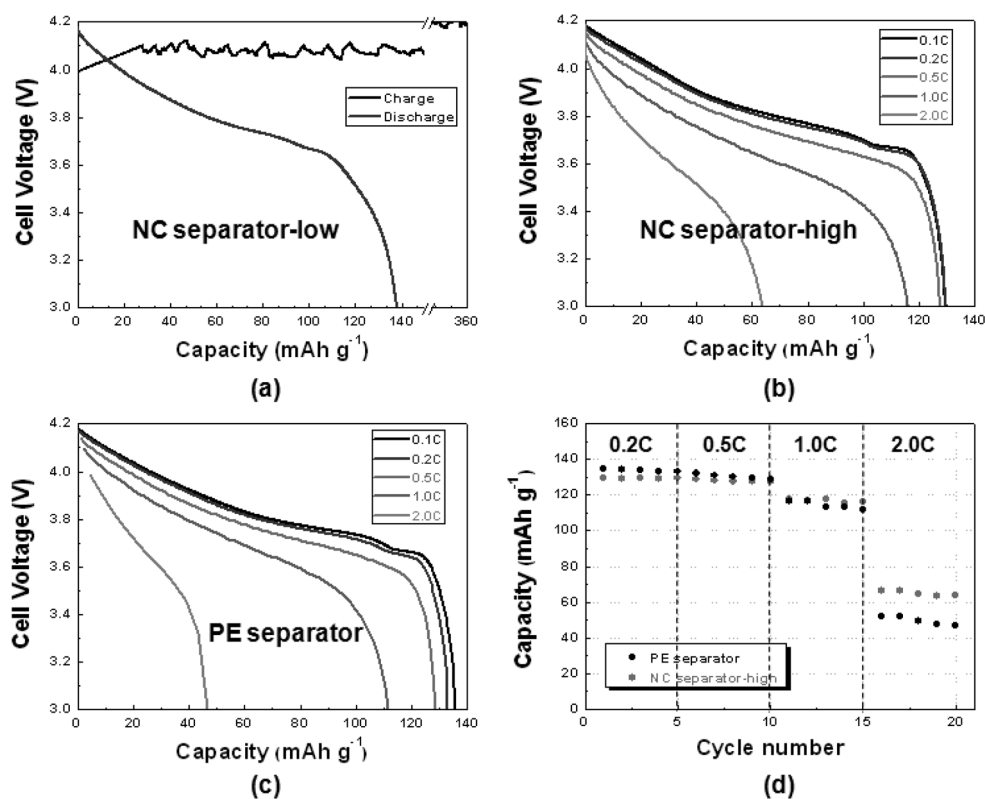


Fig. 5. Discharge profiles of cells assembled with: (a) NC separator-low; (b) NC separator-high; (c) PE separator. (d) Comparison of discharge C-rate capability between PE separator and NC separator-high.

future studies will be devoted to further characterization of electrochemical performances, including cyclability at various charge/discharge conditions, of cells assembled with the NC separator-high.

4. Conclusion

We have developed a new NC separator for a safer lithium-ion battery, which is based on the coating of SiO_2 particles/SBR binder to a PET nonwoven support. A notable feature of the NC separator was its unusual porous structure, i.e. the interstitial voids formed between the close-packed SiO_2 particles being interconnected by SBR binders. The PET nonwoven served as a mechanical support to suppress the thermal shrinkage of the composite nonwoven separator. The porous structure, Gurley value, and electrolyte wettability of NC separators were extensively investigated as a function of SiO_2 /SBR content. In comparison to the NC separator-low, the NC separator-high presented the well-tailored porous structure, which

thus contributed to affording a normal OCV profile and also stable charge/discharge behavior. In addition, the NC separator-high showed the low Gurley value indicating highly porous structure and good liquid electrolyte wettability. As a consequence, these advantages of the NC separator-high allowed for the superior cell performance, in comparison to a conventional PE separator.

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